

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-006729

(43)Date of publication of application : 12.01.2001

(51)Int.Cl.

H01M 10/40

(21)Application number : 11-172405

(71)Applicant : MITSUBISHI CHEMICALS CORP

(22)Date of filing : 18.06.1999

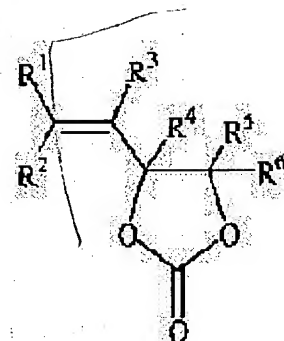
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery capable of restricting decomposition of electrolyte to the minimum, providing high capacity, and achieving excellent storage characteristics and cycle characteristics even at high temperatures.

SOLUTION: In a nonaqueous electrolyte secondary battery at least composed of a negative electrode, a positive electrode, and electrolyte comprising nonaqueous solvent and lithium salt dissolved in it, the nonaqueous solvent contains vinyl ethylene carbonate compound represented by a formula by 0.01-20 wt.%. In the formula, R¹, R², R³, R⁴, R⁵, and R⁶ refer to alkyl groups of a hydrogen atom number or carbon number of 1-4, respectively.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than

the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a nonaqueous electrolyte rechargeable battery. In detail, it is related with the nonaqueous electrolyte rechargeable battery using the electrolytic solution containing a specific vinyl ethylene carbonate compound. The cell of this invention suppresses disassembly of the electrolytic solution to the minimum, and while a high capacity is obtained, the preservation property and the cycle property are excellent under the elevated temperature.

[0002]

[Description of the Prior Art] Development of a lithium secondary battery with a high energy density is furthered with lightweight-izing of an electric product in recent years, and a miniaturization. Moreover, the improvement of a cell property is also demanded with expansion of Field of application of a lithium secondary battery. Research is briskly done for many years as a cell by which the rechargeable battery which uses a metal lithium as a negative electrode can attain high capacity-ization. However, a metal lithium grows in the shape of a dendrite by the repeat of charge and discharge, finally reaches a positive electrode and has the problem that a short circuit will arise in the interior of a cell. This problem is the biggest technical technical problem at the time of putting a metal lithium secondary battery in practical use. Then, the nonaqueous electrolyte rechargeable battery which used occlusion and the carbonaceous ingredient which can be emitted is proposed in lithium ions, such as corks, an artificial graphite, and a natural graphite, by the negative electrode. In such a nonaqueous electrolyte rechargeable battery, since a lithium does not exist in the state of a metal, formation of a dendrite is controlled, and a battery life and safety can be improved.

[0003] Especially graphite system carbon materials, such as an artificial graphite and a natural graphite, are expected as an ingredient which can raise the energy density per unit volume. However, in the nonaqueous electrolyte rechargeable battery which was independent about the various electrode material of a graphite system, or mixed the lithium with occlusion and other negative-electrode material which can be emitted, and was used as the negative electrode, if the electrolytic solution which uses as the main solvent the propylene carbonate used with a lithium primary cell, being fond generally is used, the decomposition reaction of a solvent will advance violently on a graphite-electrode front face, and the occlusion of the smooth lithium to a graphite electrode and emission will become impossible. On the other hand, since there is little such decomposition, ethylene carbonate is used abundantly as a main solvent of the electrolytic solution of a nonaqueous electrolyte rechargeable battery. However, in order that the electrolytic solution might decompose [in / as a main solvent / a charge-and-discharge process] ethylene carbonate in an electrode surface, there were problems, such as decline in charge-and-discharge effectiveness and a fall of a cycle property.

[0004] For this reason, the compound which has the carbon-carbon bonding of the partial saturation which cannot react easily with a lithium as a solvent in the nonaqueous electrolyte cell which used the lithium metal for the negative electrode in a chain type, for example, the electrolytic solution using vinyl ethylene carbonate, is proposed by JP,4-87156,A. Moreover, in the lithium cell which used the graphite

system negative electrode, in order to control disassembly of the electrolytic solution, the electrolytic solution containing vinylene carbonate and its derivative is proposed by JP,8-45545,A.

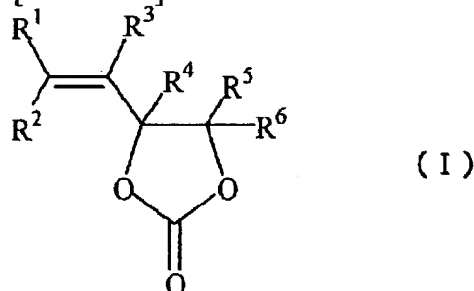
[0005]

[Problem(s) to be Solved by the Invention] However, about the electrolytic solution indicated by said official report, although the effectiveness which was excellent as it is seen, satisfaction does not go. This invention is made that this trouble should be solved, suppresses disassembly of the electrolytic solution of the nonaqueous electrolyte rechargeable battery using the negative electrode containing a carbonaceous ingredient to the minimum, its charge-and-discharge effectiveness is high, and it aims at offering the nonaqueous electrolyte rechargeable battery of the high energy consistency which excelled [bottom / of an elevated temperature] in the preservation property and the cycle property.

[0006]

[Means for Solving the Problem] this invention persons by using the electrolytic solution which contains a specific vinyl ethylene carbonate compound as the electrolytic solution of the nonaqueous electrolyte rechargeable battery using the negative electrode containing a carbonaceous ingredient as a result of inquiring wholeheartedly in view of this situation The coat with sufficient stability generated efficiently with lithium ion permeability on the negative-electrode front face from the time of early charge, and it was thought that disassembly of too much electrolytic solution was controlled, and it finds out raising charge-and-discharge effectiveness, a preservation property, and a cycle property, and came to complete this invention. That is, the summary of this invention is a nonaqueous electrolyte rechargeable battery [0007] characterized by said non-aqueous solvent containing the vinyl ethylene carbonate compound expressed with a general formula (I) at 0.01 - 20% of the weight of a rate in the nonaqueous electrolyte rechargeable battery which consists of a negative electrode, a positive electrode, and the electrolytic solution that comes to dissolve lithium salt in a non-aqueous solvent at least.

[Formula 2]



[0008] (R1, R2, R3, R4, R5, and R6 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively)

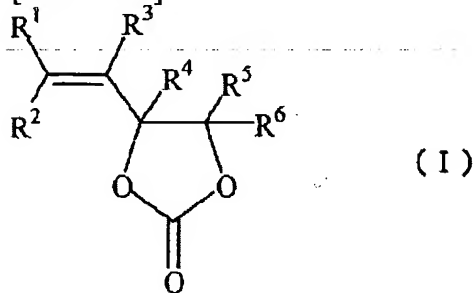
[0009] it is alike.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The nonaqueous electrolyte rechargeable battery of this invention is characterized by the nonaqueous solvent containing the vinyl ethylene carbonate compound expressed with a formula (I).

[0011]

[Formula 3]



[0012] (R1, R2, R3, R4, R5, and R6 express independently a hydrogen atom or the alkyl group of carbon numbers 1-4 among a formula, respectively)

[0013] It sets at a ceremony (I) and is R1, R2, R3, R4, and R5. And R6 When it is the alkyl group of carbon numbers 1-4, as the example, a methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, sec-butyl, i-butyl, and tert-butyl are mentioned. A methyl group and an ethyl group are desirable in these. and as an example of a vinyl ethylene carbonate compound expressed with such a formula (I) For example, 4-ethenyl -1, 3-dioxolane-2-ON (it may be called vinyl ethylene carbonate), The 4-ethenyl-4-methyl -1, 3-dioxolane-2-ON, 4-ethenyl-4-ethyl -1, 3-dioxolane-2-ON, The 4-ethenyl-4-n-propyl -1, 3-dioxolane-2-ON, The 4-ethenyl-5-methyl -1, 3-dioxolane-2-ON, 4-ethenyl-5-ethyl -1, 3-dioxolane-2-ON, the 4-ethenyl-5-n-propyl -1, 3-dioxolane-2-ON, etc. can be mentioned. Especially, vinyl ethylene carbonate, the 4-ethenyl-4-methyl -1, and 3-dioxolane-2-ON are desirable, and especially vinyl ethylene carbonate is desirable.

[0014] In addition, about the compound of a formula (I), you may have the substituent in the range which does not check the expected effectiveness of this invention too much. and the compound of a formula (I) -- the content in a non-aqueous solvent -- usually -- it is 0.1 - 5 % of the weight more preferably 0.01 to 10% of the weight 0.01 to 20% of the weight. If formation of sufficient protective coating is not made with the content being less than 0.01 % of the weight and 20 % of the weight is exceeded, the viscosity of the electrolytic solution will become high, electrical conductivity will become low, and the engine performance of a cell will fall.

[0015] As non-aqueous solvents other than the compound of a formula (I) used for this invention Annular carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate Chain-like carbonate, such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate Cyclic ester, such as gamma-butyrolactone and gamma-valerolactone, methyl acetate, Chain-like ester, such as methyl propionate, a tetrahydrofuran, 2-methyl tetrahydrofuran, Sulfur-containing organic solvents, such as chain-like ether, such as cyclic ether, such as tetrahydropyran, dimethoxyethane, and dimethoxymethane, sulfolane, and diethyl sulfone, etc. are mentioned. Two or more kinds may be mixed and these solvents may be used. What is the mixed solvent with which the chain-like carbonate chosen from the group which a non-aqueous solvent becomes from the annular carbonate chosen from the group which the carbon number of an alkylene group except the vinyl ethylene carbonate compound of a formula (I) becomes from the alkylene carbonate of 2-4, and the dialkyl carbonate whose carbon numbers of an alkyl group are 1-4 is contained more than 20 capacity %, respectively, and these carbonate occupies more than the whole 70 capacity % here is desirable.

[0016] In addition, with capacity % in this specification, all are measured at a room temperature, i.e., 25 degrees C. However, at 25 degrees C, about a solid thing, it shall heat to the melting point and shall measure in the state of melting. The carbon number of an alkylene group can mention ethylene carbonate, propylene carbonate, butylene carbonate, etc. as an example of the alkylene carbonate of 2-4, for example, and ethylene carbonate and propylene carbonate are desirable in these.

[0017] As an example of the dialkyl carbonate which is 1-4, the carbon number of an alkyl group can mention dimethyl carbonate, diethyl carbonate, G n-propyl carbonate, ethyl methyl carbonate, methyl-n-propyl carbonate, ethyl-n-propyl carbonate, etc. Dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are desirable in these. In addition, solvents other than carbonate may be contained in a mixed non-aqueous solvent.

[0018] Lithium salt is used as a solute of the electrolytic solution used by this invention. Although especially limitation will not be carried out if it can be used as a solute about lithium salt, as the example for example, LiClO₄, LiPF₆, and LiBF₄ from -- the inorganic lithium salt or LiCF₃ SO₃ chosen -- LiN (CF₃ SO₂)₂, LiN (CF₃ CF₂ SO₂)₂, LiN (CF₃ SO₂) (C₄ F₉ SO₂), and LiC(CF₃ SO₂)₃ etc. -- fluorine-containing organic lithium salt is mentioned. The inside of these, and LiPF₆ and LiBF₄ It is desirable. In addition, two or more kinds may be mixed and these solutes may be used. As for the lithium salt mol concentration of the solute in the electrolytic solution, it is desirable that it is 0.5-2 mols/l. When exceeding 1. in less than 0.5 mols [1.] /or two mols /, the conductivity of the electrolytic solution is low,

and since the engine performance of a cell falls, it is not desirable.

[0019] Although a lithium will not be limited as an ingredient of the negative electrode which constitutes the cell of this invention especially if occlusion and the carbonaceous ingredient which may be emitted are included, as the example, the pyrolysis object of the organic substance in various pyrolysis conditions, an artificial graphite, a natural graphite, etc. are mentioned, for example. Although the ingredient which performed various surface treatment which contains a pitch in the artificial graphite manufactured by elevated-temperature heat treatment of the ***** pitch suitably obtained from various raw materials and purification natural graphites, or these graphites is mainly used, these graphite ingredients have that desirable 0.335-0.34nm (distance between layers) of whose d values of the lattice plane (002nd page) for which it asked by the X diffraction by the **** method is 0.335-0.337nm more preferably. As for these graphites ingredient, it is desirable that the microcrystal size (Lc) for which ash content is 0.1 or less % of the weight, and asked by the X diffraction by the **** method 0.5 or less % of the weight more preferably 1 or less % of the weight is 30nm or more.

[0020] Furthermore, 50nm or more of microcrystal size (Lc) is more more desirable, and what is 100nm or more is the most desirable. Moreover, the median size of a graphite ingredient is a median size by the method of laser diffracting / being scattered about, and is 7-30 micrometers still more preferably 5-40 micrometers more preferably 3-50 micrometers 1-100 micrometers. the BET adsorption method specific surface area of a graphite ingredient -- 0.5-25.0m² / g -- it is -- desirable -- 0.7-20.0m² / g -- more -- desirable -- 1.0-15.0m² / g -- they are 1.5-10.0m² / g still more preferably. moreover In the Raman spectrum analysis using Ar-ion-laser light The peak PA of the range of 1580-1620cm⁻¹ (Peak intensity IA) And intensity ratio R=IB of the peak PB (peak intensity IB) of the range of 1350-1370cm⁻¹ / IA The full width at half maximum of the range of zero to 0.5 and 1580-1620cm⁻¹ One or less [26cm⁻¹ -] As for the full width at half maximum of the range of 1580-1620cm⁻¹, one or less [25cm⁻¹ -] is more desirable.

[0021] Moreover, the negative-electrode material which emits [occlusion and] a lithium can also be mixed and used for these carbonaceous ingredients. As negative-electrode material which emits [occlusion and] lithiums other than a carbonaceous ingredient, metallic-oxide ingredients, such as tin oxide and oxidization silicon, and the lithium alloy of versatility [list / lithium metal] further can be illustrated. Two or more kinds may be mixed and these negative-electrode ingredients may be used. It is not limited especially about the method of manufacturing a negative electrode using these negative-electrode ingredients. For example, it can apply to the substrate of a charge collector, and by drying, a negative electrode can be manufactured and roll forming of this negative-electrode ingredient is carried out as it is, and a binder, a thickener, electric conduction material, a solvent, etc. can be added to a negative-electrode ingredient if needed, and it can consider as the shape of a slurry, and can also consider [it can consider as a sheet electrode or] as a pellet electrode with compression molding.

[0022] About the binder used for manufacture of an electrode, to the solvent or the electrolytic solution which are used at the time of electrode manufacture, if it is a stable ingredient, it will not be limited especially. As the example, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. can be mentioned. As a thickener, a carboxymethyl cellulose, methyl cellulose, a hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidization starch, phosphorylation starch, casein, etc. are mentioned. As electric conduction material, carbon materials, such as metallic materials, such as copper and nickel, graphite, and carbon black, are mentioned.

[0023] The quality of the material of the charge collector for negative electrodes has the point of metals, such as copper, nickel, and stainless steel, being used and being easy to process it into a thin film in these, and the point of cost to desirable copper foil. As an ingredient of the positive electrode which constitutes the cell of this invention, the ingredient which emits [occlusion and] lithiums, such as lithium transition-metals multiple oxide ingredients, such as lithium cobalt oxide, a lithium nickel oxide, and a lithium manganic acid ghost, can be used. Especially about the manufacture approach of a positive electrode, it is not limited but can manufacture according to the manufacture approach of the above-mentioned negative electrode. Moreover, about the configuration, after mixing, a binder, electric conduction material, a solvent, etc. can be added to a positive-electrode ingredient if needed, and it

applies to the substrate of a charge collector, and it can consider as a sheet electrode or can consider [press forming can be performed and] as a pellet electrode. As for the quality of the material of the charge collector for positive electrodes, metals, such as aluminum, titanium, and a tantalum, or the alloy of those is used. In these, since especially aluminum or its alloy is lightweight, it is desirable in respect of energy density.

[0024] It is not limited especially about the quality of the material or the configuration of a separator which are used for the cell of this invention. However, it is stable to the electrolytic solution, and choosing from the solution retention outstanding ingredients is desirable, and it is desirable to use a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material. Especially about the method of manufacturing the cell of this invention which has a negative electrode, a positive electrode, and a nonaqueous electrolyte at least, it is not limited but can choose suitably from the approaches usually adopted. Moreover, the coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which were not limited especially about the configuration of a cell but made the sheet electrode and the separator the shape of a spiral is usable.

[0025]

[Example] Although an example and the example of a comparison are given to below and this invention is explained to it still more concretely, this invention is not limited to these examples, unless the summary is exceeded.

[0026] (Example 1) About the electrolytic solution, vinyl ethylene carbonate is dissolved in propylene carbonate at 5% of the weight of a rate, using as a solute the 6 phosphorus-fluoride acid lithium (LiPF₆) which fully dried under the desiccation argon ambient atmosphere, and it is LiPF₆ further. It dissolved and prepared at a rate of one mol/l. d value of the lattice plane (002nd page) in an X diffraction 0.336nm and crystallite size (Lc) The median size according [100nm or more (264nm) and ash content] to the method of laser diffracting / being scattered about 0.04% of the weight 17 micrometers, BET adsorption method specific surface area 8.9m² g, In the Raman spectrum analysis using Ar-ion-laser light The peak PA of the range of 1580-1620cm⁻¹ (Peak intensity IA) artificial-graphite powder KS-44 [and] (the TIMCAL, LTD. make --) whose full width at half maximum of the range of 0.15 and 1580-1620cm⁻¹ intensity ratio R=IB of the peak PB (peak intensity IB) of the range of 1350-1370cm⁻¹ / IA is 22.2cm⁻¹ In addition, the styrene butadiene rubber (SBR) which the trade name 94 weight section was made to distribute with distilled water is mixed by the De Dis parser so that it may become 6 weight sections by solid content. What was made into the shape of a slurry is applied to homogeneity on copper foil with a thickness of 18 micrometers which is a negative-electrode charge collector. After desiccation, it pierced to discoid with a diameter of 12.5mm, and the electrode was produced, it considered as the operation pole and the coin mold half cel constituted considering the lithium foil as a counter electrode through the separator into which the electrolytic solution was infiltrated was produced.

[0027] (Example 1 of a comparison) Vinylene carbonate is dissolved in propylene carbonate at 5% of the weight of a rate, and it is LiPF₆ further. The coin mold half cel was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

(Example 2 of a comparison) To propylene carbonate, it is LiPF₆. The coin mold half cel was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0028] (Example 2) Vinyl ethylene carbonate is dissolved in the mixture (1:1 capacity factors) of ethylene carbonate and diethyl carbonate at 2% of the weight of a rate, and it is LiPF₆ further. The coin mold half cel was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0029] (Example 3 of a comparison) It is LiPF₆ to the mixture (1:1 capacity factors) of ethylene carbonate and diethyl carbonate. The coin mold half cel was produced like the example 1 except having used the electrolytic solution dissolved and prepared at a rate of one mol/l.

[0030] Next, in 25 degrees C, the charge and discharge test was performed by 0.2mA constant current

charge termination electrical-potential-difference 1.5V according to constant current (discharge-final-voltage 0V and 0.4mA) about the coin mold half cell of the examples 1 and 2 produced as mentioned above and the examples 1-3 of a comparison. Moreover, about examples 1 and 2 and the example 3 of a comparison, after saving at 60 degrees C in the state of a dope after 10 cycles for 48 hours, it was made to dedope and the preservation property was examined. The capacity-potential curve accompanying the charge and discharge of 1 cycle eye of an example 1 and the examples 1 and 2 of a comparison is shown in drawing 1, and 2 and 3. Capacity shows the capacity per [which was used as an operation pole] graphite weight here. Moreover, the dedope capacity (dedope capacity of the lithium from an operation pole) and effectiveness (dedope capacity x100-/dope capacity) of 1 cycle eye of examples 1 and 2 and the examples 1-3 of a comparison are shown in Table 1. As a preservation property, the percentage of the capacity after preservation (dedope capacity of 11 cycle eye) to the capacity before preservation of examples 1 and 2 and the example 3 of a comparison (dedope capacity of 10 cycle eye) is shown in Table 2.

[0031] As shown in drawing 3, in the case of a propylene carbonate independent solvent, a flat part is observed by the 0.8V neighborhood, disassembly of the electrolytic solution advances, and a dope is impossible to 0V. Decomposition control is not enough although a dope will become possible to 0V, if the electrolytic solution containing vinylene carbonate is used as shown in drawing 2. Disassembly of too much electrolytic solution is controlled by using the electrolytic solution which contains vinyl ethylene carbonate as shown in drawing 1. It is distinct that effectiveness is excellent while the direction at the time of using the electrolytic solution containing vinyl ethylene carbonate from Tables 1 and 2 maintains a high capacity, and the preservation property under an elevated temperature also improves.

[0032]

[Table 1]

表 1

	1 サイクル目脱ドープ容量 (mA h / g)	1 サイクル目効率 (%)
実施例 1	3 2 7	9 1. 6
実施例 2	3 1 4	9 1. 6
比較例 1	3 1 5	6 6. 6
比較例 2	—	—
比較例 3	3 1 8	9 1. 2

[0033]

[Table 2]

表 2

	保存特性 (%)
実施例 1	9 7. 6
実施例 2	9 7. 1
比較例 3	9 6. 7

[0034]

[Effect of the Invention] In the nonaqueous electrolyte rechargeable battery equipped with the negative

electrode containing a carbonaceous ingredient, while suppressing disassembly of the electrolytic solution to the minimum and obtaining a high capacity by using the non-aqueous solvent containing the vinyl ethylene carbonate compound expressed with a formula (I), the cell which was excellent in the preservation property and the cycle property under the elevated temperature can be produced, and it can contribute to the miniaturization of a nonaqueous electrolyte rechargeable battery, and high performance-ization.

[Translation done.]